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14. ABSTRACT
Synthetic approaches to racemic and enantiomerically pure helical oligomers (helicenes)were developed. The molecular shape of the oligomers were modified with substituents to control the solid state packing; one of such oligomers was found to form a nearly isotropic chiral molecular glass with a significant rotatory power.

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FINAL REPORT

Technical Section

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Technical Objectives

The primary objective of this project is the synthesis of organic materials for chiral guiding layers in planar optical waveguides. Such a material would preferably be an organic polymer or oligomer, readily forming isotropic, amorphous thin films with relatively high bulk rotatory power ($|\alpha|$), approaching 100 deg/mm. This large optical rotation must occur in the optically transparent and devoid of scattering wavelength range, including $\lambda = 633$ nm for the current testing (HeNe laser), and in the NIR range for future applications. The requirement for an isotropic film is important because linear birefringence, which could arise from unwanted ordering/aggregation of polymer chains, may easily overwhelm the circular birefringence; even for a huge $|\alpha| = 500$ deg/mm at $\lambda = 633$ nm, circular birefringence, $|n_L - n_R|$, is only about 2×10^{-3}. Furthermore, a chiral polymer/oligomer must be thermally stable at 85 °C for a minimum of several years.

Technical Approach

Our preliminary data showed that tetranaphthalene (+)-**1** forms isotropic glasss with a modest rotatory power (Figure 1). In order to increase the rotatory power, [n]helicenes were selected as initial target materials. Because the especially strong strong chiral, especially chirooptical, properties of [n]helicenes are greatly enhanced with increasing number (n) of *ortho*-annelated aromatic rings, synthetic methodology for highly-functionalized [n]helicenes was required. The adequate functionalization of helicenes is needed for the following reasons: (1) solid-state engineering to obtain glassy material, (2) adequate solubility in organic solvents for processing, and (3) synthesis of higher [n]helicene homologues and helicene-based polymers. The target materials are highly-functionalized [7]helicenes **2** and **3**, and [5]helicene **8**, related to the $(C_2S)_n$ carbon-sulfur helix (Figure 1).

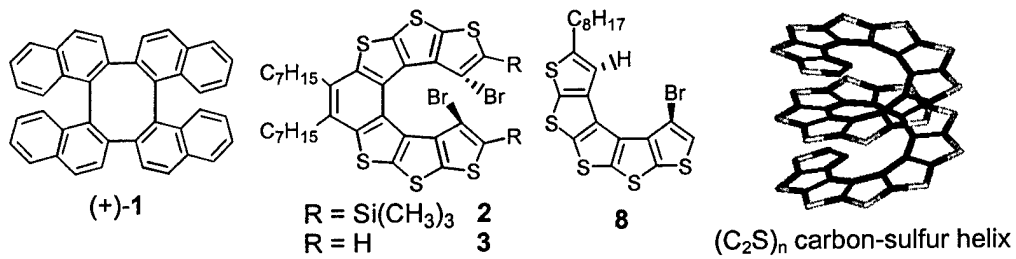
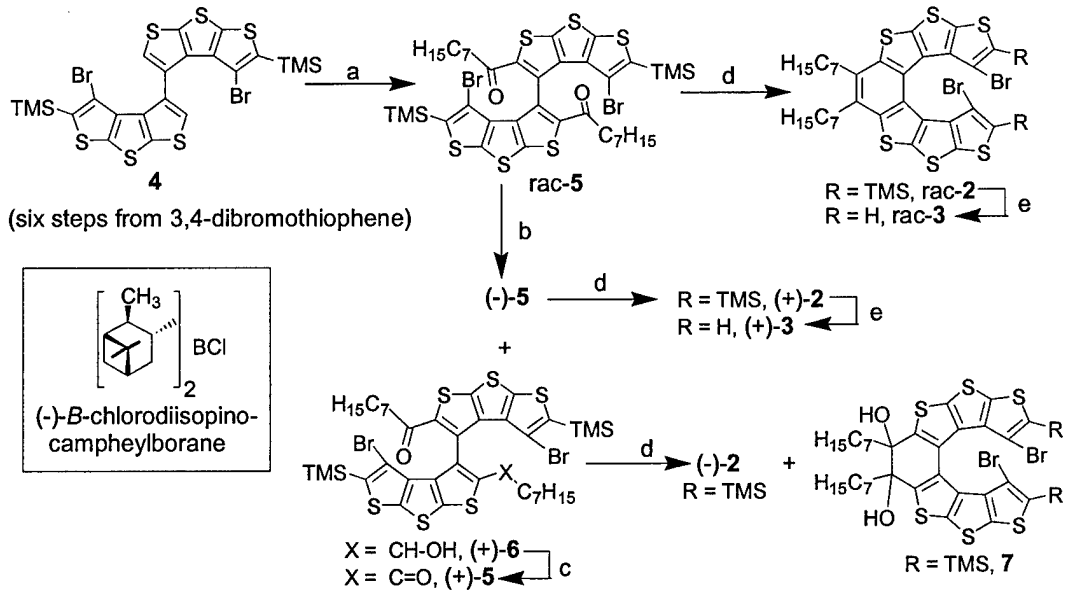


Figure 1. Tetranaphthalene (+)-**1** and the target helicenes **2**, **3**, and **8**.

Progress

Our technical progress is described in detail in references 1 and 2. The key findings are summarized below.

Synthesis and characterization of di-functional helicenes 2 and 3.[1] The LDA-mediated dilithiation of **4** (prepared in several steps in the PI's laboratory) at the unprotected α-positions is followed by addition of *N*-methoxy-*N*-methyloctanamide to provide racemic diketone (rac-**5**) in 54 – 65% yield (Scheme 1). Using (–)-*B*-chlorodiisopinocampheylborane, kinetic resolution of rac-**5** is carried out till approximately 50% conversion to alcohol **6** (~3 days at 45 – 50 °C). The unreacted diketone (–)-**5** is isolated in ~40% yield. Oxidation of alcohol (+)-**6** with PCC gives diketone (+)-**5** in 80 – 92% yield (or ~40% yield based upon rac-**5**). Enantiomeric excess (ee) for both (–)-**5** and (+)-**5** is in the 70 – 80% ee range, as determined by HPLC analysis.[22] Treatment of nonracemic (+)-**5** ($[\alpha]_D^{rt}$ = +91) with ether gives enantiopure diketone (+)-**5** ($[\alpha]_D^{rt}$ = +134, 99+ % ee) in 21% yield (based upon alcohol **6**), as ether soluble fraction.



Scheme 1. Reagents and conditions: a) LDA, ether, *N*-methoxy-*N*-methyloctanamide, 54 – 65%; b) (–)-*B*-chlorodiisopinocampheylborane, ether, 40% (for (–)-**5** with 70 – 80% ee), 40% (for (+)-**6** with 70 – 80% ee); c) PCC, CH_2Cl_2, 80 – 92%; d) $TiCl_3$, Zn, DME, 38% (for rac-**2** from rac-**5**), 17 – 63% (for (+)-**2** with ~50 – 90% ee from (–)-**5** with 71 – 91% ee), ~28% (for (–)-**2** with ~74% ee (NMR) from (+)-**5** with 56% ee); e) TFA, chloroform, 94% (for rac-**3**).

The intramolecular McMurry reaction of diketone **5**, using $TiCl_3$-Zn-DME, gives the target [7]helicene **2** in 17 – 63% yield (Scheme 1). The wide range of the isolated yields for **2** is associated with the formation of diol **7** (and its de-silylated derivatives); in particular, the *trans* isomer of **7** is expected to be unreactive toward the deoxygenation to the corresponding "olefin", i.e., [7]helicene **2**. The ^{1}H NMR analyses of the crude reaction mixtures suggest that the overall yield for the ring closure (**2** + **7**) is nearly constant (70 – 80%); however, the relative content of **2** vs. **7** has a wide distribution (Table 1s, Supporting Information).

Fractional crystallization of nonracemic **2** from isopropanol/ether gives pure enantiomers; for example, (+)-**2** with ~50% ee gives (+)-**2** with 99% ee ($[\alpha]_D^{rt}$ = +1166) in nearly quantitative yield (or 19% yield based upon diketone **5**). Deprotection of the TMS group gives [7]helicene **3** (Scheme 1).

The structures of rac-**2**, rac-**3**, and (+)-**3** are confirmed by the X-ray crystallographic analyses (Figure 2). (Synchrotron source at the Advanced Photon Source at Argonne has been used to collect X-ray data for rac-**3** and (+)-**3**.) Excluding different conformations and crystallographic disorder of the alkyl chains, the molecules in all three crystals show approximate C_2-symmetry. Determinations of the absolute configuration for [7]helicene (+)-**3** indicate the (*P*) helical chirality, which is consistent with the positive $[\alpha]_D^{rt}$ usually found for (*P*) [n]helicenes. The crystal of rac-**3**, which was selected for the X-ray crystallographic analysis, was found to be essentially identical to that of (+)-**3**, except for its (*M*) helical chirality. This indicates that crystals of rac-**3**, which are obtained from isopropanol/benzene, correspond to a conglomerate, i.e., each enantiomer crystallizes separately.

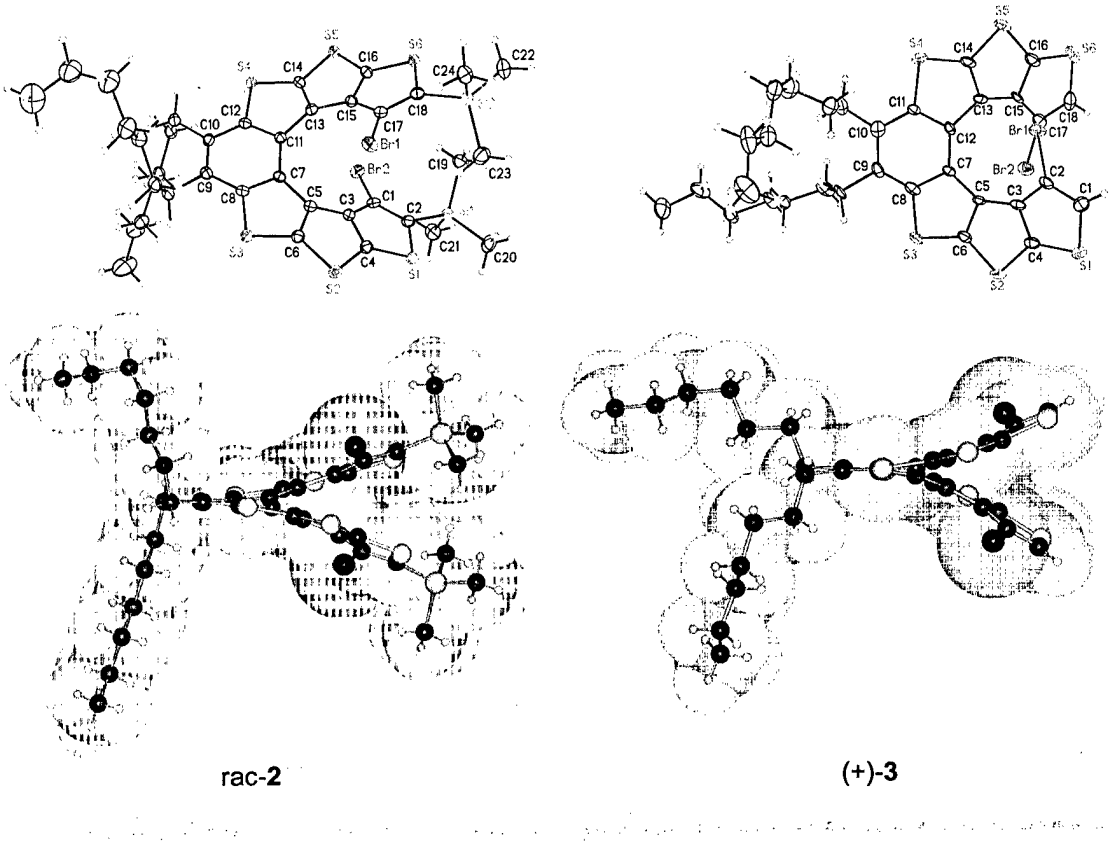


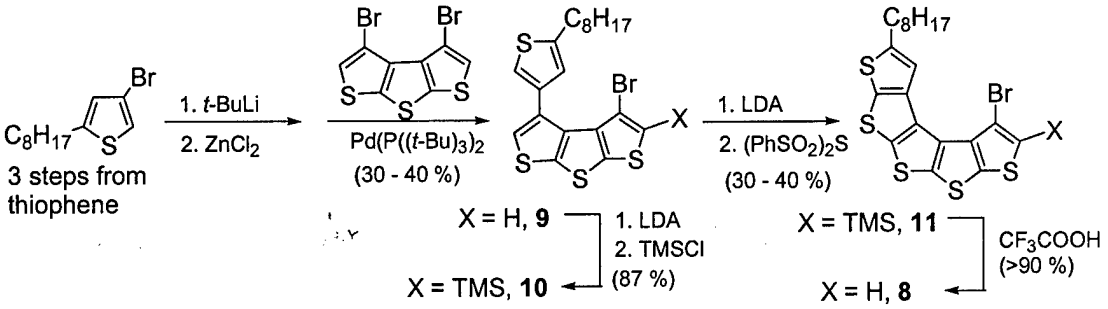
Figure 2. Molecular structure and conformation for [7]helicenes rac-**2** (left plots) and (+)-**3** (right plots). (Structure of rac-**3** is not shown.) Atom numbering and disorder for the C_7-alkyl chains are omitted for clarity. In the ortep plots, all atoms, except for the hydrogens are depicted with thermal ellipsoids set at the 50% probability level.

Differential scanning calorimetric (DSC) analyses of racemic and enantiopure helicenes **2** and **3** indicate that (+)-**2** helicene shows glass-like endothermic transition ($\Delta H = 3 - 4$ kJmol^{-1}) with an onset at 61±1 °C. All other [7]helicenes studied here showed well-defined melting transitions.

The glassy behavior may in principle be associated with inefficient crystal packing of molecules. It is well known that among 230 crystallographic space groups, only 65 space groups are compatible with enantiopure molecules. In particular, the absence of the inversion centers and/or glide reflections, which are precluded for crystals of enantiopure molecules, may lead to unfavorable interactions from juxtaposed polar groups. For small, achiral organic molecules, the difficulty in crystallization may typically be associated with rigid, "tetrahedral-like" shapes. Both **2** and **3** adopt four-armed chiral shapes

(including "flexible" alkyl groups) in the crystals (Figure 2); possibly, with the trimethylsilyl groups, the shape of **2** approaches closer to "tetrahedral-like". These minute molecular shape differences lead to different crystal packings of rac-**2** and **3**, and might contribute to glass-like behavior of enantiopure **2**.

Synthesis of mono-functional helicene 8.[2] Synthesis of racemic [5]helicene **8** is summarized in Scheme 2. The key CC bond forming step involves cross-coupling between thiophene moieties at their



Scheme 2. Mono-functional helicene **8**.

beta-positions. In general, coupling at this position in thiophene is considered difficult even when only one partner is a thiophene. We modified and optimized the reaction conditions for such cross-coupling, starting from a version of a Negishi coupling reported by Fu and coworkers. The key example is shown in the first step of the synthesis in Scheme 2. In-situ ^{1}H NMR spectroscopic follow-up of the reaction mixture of **10** with LDA is required to obtain 30 – 40 % yields for the closure to [5]helicene **11**. We found that [5]helicene **8** readily racemizes at room temperature.[2] Such low barrier for racemization and the functionalization facilitates the use of this [5]helicene for synthesis of higher helicenes.

Most recently, after the end of the present funding period, we succeeded in cross-coupling of [5]helicene **8**, followed by asymmetric annelation to the corresponding di-octyl-substituted [11]helicene (ca. 20% enantiomeric excess). This illustrates the potential of the synthetic approaches developed here for syntheses of higher helicenes, which should possess the required level of rotatory power.

Coordination with the Navy

Transparent film of [7]helicene (+)-**2** on a glass slide has been prepared by casting from cyclohexanone in the PI's laboratory in December of 2003, and then shipped to Dr. W. N. Herman's laboratory (Department of the Navy, EO Sensors Division, AIR 456, NAWCAD, Patuxent River, Maryland 20670) for preliminary optical studies. The results of those studies are summarized, as communicated to the PI by Dr. W. N. Herman: the film is nearly isotropic with $\Delta n \approx 0.0003$ in the $\lambda =$ 630 – 1550 nm range; rotatory power of 11 deg/mm (at 670 nm) and 6.0 deg/mm (at 850 nm) are obtained. For reference, the optical rotation in solution is $[\alpha]_D^{rt} = +1166$.

These results may be compared to the first generation material, tetranaphthalene (+)-**1**, submitted for preliminary testing by the PI in 2002. The film, which has been spincoated at the Dr. Herman's laboratory, was found to be isotropic within experimental error ($\Delta n = \pm 0.0005$), with rotatory power of 8.7 deg/mm (at 633 nm). For reference, the optical rotation in solution was $[\alpha]_D^{rt} = +430$.

Conclusion

Synthetic methodologies for novel highly-functionalized [7]helicenes and [5]helicenes are developed. Both helicenes are exceptionally suited to serve as building blocks for higher helicenes and polymers with high rotatory powers. A unique, glass-forming, enantiomerically-pure [7]helicene was

obtained and characterized. Its rotatory power in the thin film is significantly improved compared to the original tetranaphthalene (+)-**1**.

References (publications resulting from the ONR support)

1. M. Miyasaka, A. Rajca, M.Pink, S. Rajca, "Chiral Molecular Glass: Synthesis and Characterization of Enantiomerically Pure Thiophene-Based [7]Helicene." *Angew. Chem. Int. Ed.*, submitted on 3/12/04.
2. M. Miyasaka, A. Rajca, "Synthesis of a Short Carbon-Sulfur Helicene: Pd-Catalyzed Cross-Coupling at the β-Positions of Thiophenes," *Synlett* (invited cluster) **2004**, 177 – 182.